



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> C07C 235/34, 235/36 C08K 5/20, C08L 23/02	<b>A1</b>	<b>(11) International Publication Number:</b> WO 93/20040 <b>(43) International Publication Date:</b> 14 October 1993 (14.10.93)
<b>(21) International Application Number:</b> PCT/US93/02722 <b>(22) International Filing Date:</b> 19 March 1993 (19.03.93)  <b>(30) Priority data:</b> 860,795                      30 March 1992 (30.03.92)                      US  <b>(71) Applicant:</b> EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US).  <b>(72) Inventors:</b> WANG, Richard, Hsu-Shien ; 1414 Fairridge Drive, Kingsport, TN 37664 (US). SHANG, Ping, Peter ; 2549 Essex Drive, Kingsport, TN 37660 (US). JERVIS, Daniel, Alan ; P.O. Box 5631, Kingsport, TN 37663 (US).  <b>(74) Agent:</b> THOMSEN, J., Frederick; 343 State Street, Roches- ter, NY 14650-2201 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> NOVEL BIS(PHENOLIC-AMINE)QUINONE COMPOUNDS AND POLYOLEFIN COMPOSITIONS STABI- LIZED THEREWITH  <b>(57) Abstract</b>  Disclosed is a class of bis(phenolic-amine)quinone compounds which are useful as stabilizers for polyolefins. The bis(phenolic-amine)quinone compounds inhibit oxidative degradation of polyolefins which is attributable to heat and/or ultraviolet light and is promoted or accelerated by metals, e.g., copper, in contact with the polyolefin. The compounds also exhibit excellent thermal stability.		

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- 1 -

NOVEL BIS(PHENOLIC-AMINE)QUINONE COMPOUNDS  
AND POLYOLEFIN COMPOSITIONS STABILIZED THEREWITH

5        This invention pertains to certain novel  
bis(phenolic-amine)quinone compounds which are useful as  
metal deactivators and antioxidants in polyolefins.  
This invention also pertains to polyolefin compositions  
containing one or more of the bis(phenolic-amine)quinone  
compounds.

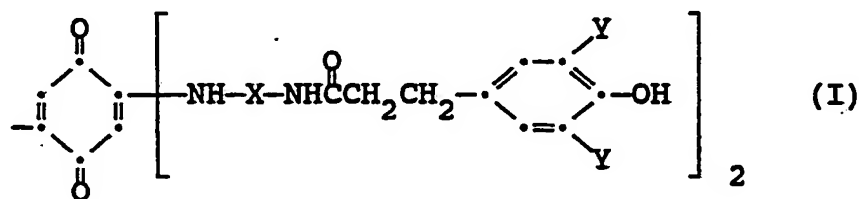
10        Poly- $\alpha$ -olefins require the presence therein of  
stabilizers to prevent or retard oxidative, thermal  
and/or ultraviolet light deterioration. The most common  
of such poly- $\alpha$ -olefins are low, medium and high density  
polymers derived from ethylene, propylene, mixtures  
15        thereof and copolymers of ethylene and minor amounts of  
higher  $\alpha$ -olefins such as 1-butene, 1-hexene, 1-octene,  
1-dodecene, etc. Stabilizers typically present in such  
poly- $\alpha$ -olefins include a phenolic antioxidant such as  
2,2-bis[[3-[3,5-bis(2-methyl-2-propyl)-4-hydroxyphenyl]-  
20        1-oxopropoxy)methyl]-1,3-propanediyl 3,5-bis(1,1-di-  
methylethyl)-4-hydroxybenzenepropanoate [Irganox  
(trademark) 1010 stabilizer] or 2,6-bis(1-methylhepta-  
decyl)-p-cresol, phosphites such as trihydrocarbyl  
phosphites including cyclic phosphites and sulfides such  
25        as thiodipropionate esters such as dilauryl thiodi-  
propionate.

When poly- $\alpha$ -olefin compositions are used as  
coatings for metals, e.g., as wire coating compositions,  
the compositions also contain a metal deactivator to  
30        inhibit polymer degradation which is promoted or  
accelerated by the metal. For example, polyolefin  
compositions used to coat copper wire typically contain  
a copper deactivator such as N,N'-dibenzaloxalyldi-  
hydrazide. For some wire coating applications, it is  
35        necessary that the metal deactivator resist leaching

- 2 -

from the polyolefin when it is in contact with such materials as petrolatum used as a filler in electrical cables. However, most commercial phenolic antioxidants such as Irganox 1010 are readily leached from the polyolefin coating by petrolatum.

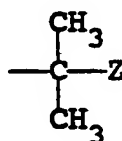
One embodiment of the present invention pertains to a class of novel bis(phenolic-amine)quinone compounds which function as both phenolic antioxidants and metal deactivators when incorporated into poly- $\alpha$ -olefins intended for use in coating metal articles, particularly copper wire. These novel compounds have the general formula:



wherein

X is alkylene or cycloalkylene; and

Y is a tertiary hydrocarbyl group having the formula



wherein Z is alkyl or aryl.

The alkylene groups which X may represent contain up to about 12 carbon. The cycloalkylene groups represented by X may contain from 4 to 7 ring carbon atoms. X preferably is alkylene of 2 to 8 carbon atoms. Examples of the alkyl groups represented by Z include alkyl containing up to about 8 carbon such as methyl, ethyl, propyl, 2-propyl, butyl, 2-butyl, 2-methyl-2-propyl, pentyl, 2-pentyl, hexyl, 2-ethyl-hexyl, 2,4,4-trimethyl-2-pentyl. The alkyl groups preferably contain up to 4

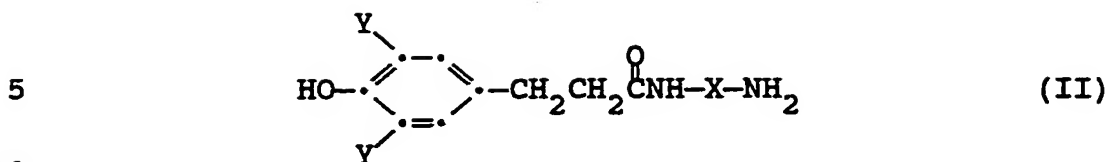
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carbon atoms. The aryl group represented by Z may be unsubstituted phenyl or phenyl substituted with 1 or 2 groups selected from lower, i.e., containing up to about 4 carbon atoms, alkyl, lower alkoxy or halogen, e.g., chlorine or bromine. Z most preferably is methyl, i.e., the hydrocarbyl group represented by Y is 2-methyl-2-propyl (tertiary butyl).

A second embodiment of the invention pertains to a polyolefin composition comprising an intimate mixture of (i) a normally-solid polymer of ethylene, propylene, a mixture of ethylene and propylene or polymers of ethylene and an  $\alpha$ -olefin having 4 to 12 carbon atoms and (ii) 1 or more compounds of formula (I) above. The concentration of the compound of formula (I) which will effectively inhibit polymer degradation can vary considerably depending on the particular polymer being stabilized and the end use for which the stabilized polymeric material is designed. Generally, concentrations in the range of 0.05 to 5.0 weight percent may be used with concentrations of about 0.1 to 1.0 being most common. The stabilizers provided by this invention may be used in combination with other conventional stabilizers such as polyvalent salts of organic acids, thioethers, phosphites and ultraviolet light stabilizers. In addition, other additives, such as plasticizers, lubricants, emulsifiers, antistatic agents, flame retardant agents, pigments and fillers, commonly used in formulating commercial polymeric compositions may be present.

The novel stabilizer compounds provided by the present invention may be prepared in accordance with conventional synthesis procedures by reacting a phenolic-amide-amine having the structure:

- 4 -



with para-benzoquinone at elevated temperatures in the presence of an inert solvent such as an alkanol. The intermediates of formula (II) may be prepared from alkyl 3-arylpropionate esters and various diamines.

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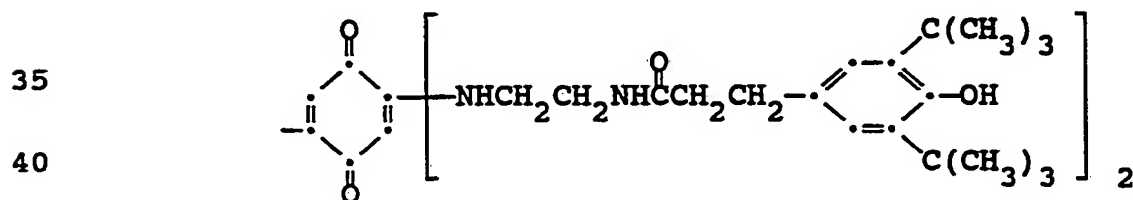
The preparation and use of the stabilizers of the invention are further illustrated by the following examples.

20 EXAMPLE 1

A solution of N-(2-aminoethyl)-3-[3,5-bis(2-methyl-2-propyl)-4-hydroxyphenyl]propionamide (0.0875 mol) in ethanol (100 mL) at 50°C is added slowly over a period of 30 minutes p-benzoquinone (0.132 mol) in ethanol (120 mL). The mixture is heated to and maintained at reflux temperature for 6 hours. The mixture then is cooled to room temperature and the product is collected by filtration, washed with acetone and dried. The product is obtained in a yield of 60% and has a melting point of 262-265°C and the structure:

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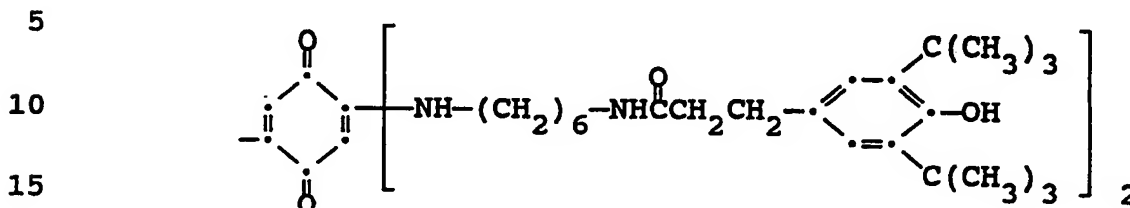
45 EXAMPLE 2

A solution of N-(6-aminoethyl)-3-[3,5-bis(2-methyl-2-propyl)-4-hydroxyphenyl]propionamide (0.0875 mol) in ethanol (100 mL) at 50°C is added slowly over a period of 30 minutes p-benzoquinone (0.132 mol) in ethanol (120 mL). The mixture is heated to and maintained at reflux temperature for 6 hours. The mixture then is cooled to

50

- 5 -

room temperature and the product is collected by filtration, washed with acetone and dried. The product is obtained in a yield of 60% and has a melting point of 80-110°C and the structure:



20 The polyolefin compositions provided by the present invention may be prepared by incorporating one or more of the bis(phenolic-amine)quinones described hereinabove into poly- $\alpha$ -olefin polymers by conventional blending techniques. For example, the bis(phenolic-amine)quinone compounds may be added directly to a melt of the poly-olefin on a roll mill to distribute the bis(phenolic-amine)quinone compound uniformly throughout the polymer.

25 Alternatively, the compounds may be dry-blended with a finely-divided form of the polyolefin such as pellets and then the dry mix can be mixed further in and

30 extruded from an extruder.

The novel polyolefin compositions of the invention are particularly useful for coating copper materials such as copper wires. Thus, a third embodiment of the present invention pertains to a coated article

35 comprising a copper material, especially copper wire, bearing a coating of one of the polyolefin compositions described herein.

#### EXAMPLE 3 AND COMPARATIVE EXAMPLE 1

40 The bis(phenolic-amine)quinone compound prepared as described in Example 1 is evaluated as a stabilizer in and for polyethylene according to the following procedure. The amounts of materials employed are given in parts by weight. The compound of Example 1 (1.2

- 6 -

parts) is dry mixed with a sample (600 parts) of unstabilized, high density polyethylene [Alathon (trademark) 7050, Oxy Chemical]. The mixture then is fed to and extruded from a C. W. Brabender conical, twin-screw extruder at 200°C over a period of 2 minutes. The extruded polyolefin composition is pelletized and the pellets are pressed into film 254 microns thick at a temperature of 200°C and a pressure of 68.95 megapascals (10,000 pounds per square inch) using a Carver laboratory press. Film also is prepared from the same high density polyethylene which did not contain any bis(phenolic-amine)quinone compound.

The stability of the film samples of the polyolefin compositions is determined by Differential Scanning Calorimetry (DSC) analysis according to the general procedure described by Ellerstein, "The Use of Dynamic Differential Calorimetry for Ascertaining the Thermal Stability of Polymers," Analytical Calorimetry, Eds., R.S. Porter and J.F. Johnson, Plenum, New York, 1968, p. 279 and by Wright, "Oxidative Stability of Expanded Polyethylene for Wire and Cable," J. Cell. Plast., 6, 317 (1976). A 3-4 mg sample of each film is placed in an aluminum or copper pan without the lid and scanned at a rate of 20°C per minute from 40 to 300°C under forced air at a rate of 15 mL per minute. Degradation of a polyolefin composition occurs at the temperature at which an oxidative exotherm is observed. The thermal oxidative degradation of polyolefins is essentially a controlled burning and thus produces heat which is detected by the DSC instrument. A stabilizer which increases the temperature at which degradation begins increases the overall usefulness of the polyolefin. The onset temperature of the oxidative exotherm curve that is measured as the degradation temperature of a sample is determined as the intercept of the baseline before



- 7 -

degradation starts and the following straight line when degradation occurs.

The temperature at which each polyolefin composition degrades, determined as described above, is shown in Table I. Degradation temperatures are given in Table I for the film samples scanned in the aluminum pan and the copper pan. It is apparent from the examples of Table I, including Comparative Example 1 (C-1), that the copper of the copper pan promotes or accelerates the degradation of the film samples of the polyolefin compositions. It also is apparent that the presence of one of the bis(phenolic-amine)quinone compounds of the present invention in the polyethylene improves the stability thereof by raising the temperature at which the polyolefin composition degrades, as determined in both the aluminum (Al) pan and in the copper (Cu) pan.

TABLE I

Example	<u>Degradation Temperature, °C</u>	
	<u>Al Pan</u>	<u>Cu Pan</u>
C-1	239	220
1	261	260

The thermal stability of the bis(phenolic-amine)-quinone compounds prepared as described in Examples 1 and 2 is determined by thermogravimetric analysis and compared with the thermal stability of a known phenolic-hydrazide metal deactivator, N,N'-bis[3-[3,5-bis(2-methyl-2-propyl)-4-hydroxyphenyl]propionyl]hydrazide (MD-1024). A sample of each compound was placed in a thermobalance and heated at a rate of 20°C per minute from 25°C to 600°C. The heating was performed in both air and in a nitrogen atmosphere. The weight loss of each sample is recorded as a function of temperature.

- 8 -

The temperatures at which the samples have lost 5 weight percent of their weight are:

Compound of Example 1: 325°C in nitrogen

315°C in air

5 Compound of Example 2: 325°C in nitrogen

305°C in air

MD-1024: 290°C in nitrogen

290°C in air

10 The above data show that the thermal stability of the bis(phenolic-amine)quinone compounds of the present invention is superior to that of the known phenolic-hydrazide compound MD-1024.

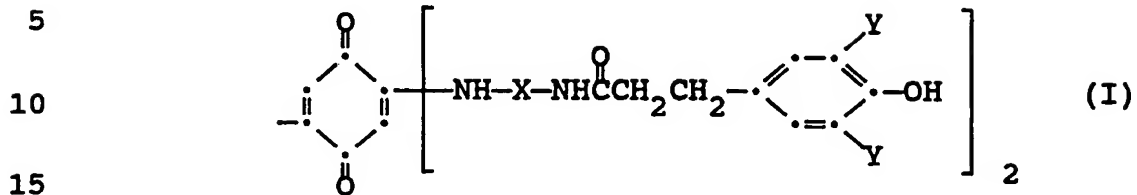
15 The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications may be effected within the spirit and scope of the invention.

- 9 -

CLAIMS

We claim:

1. A compound having the formula:



wherein

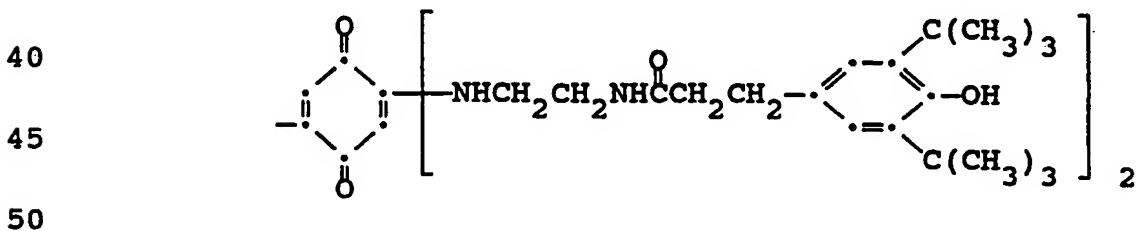
X is alkylene or cycloalkylene; and

- 20 Y is a tertiary hydrocarbyl group having the formula

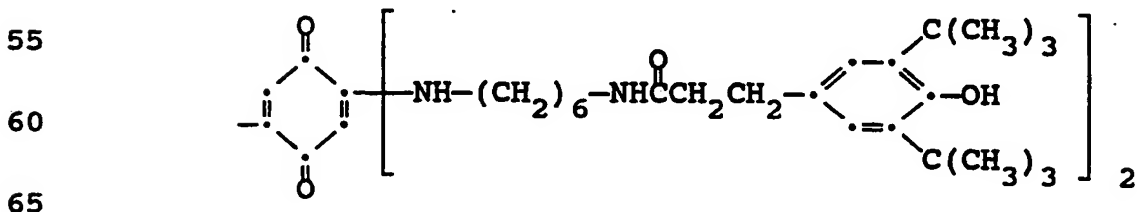


wherein Z is alkyl or aryl.

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2. A compound according to Claim 1 having the formula



3. A compound according to Claim 1 having the formula



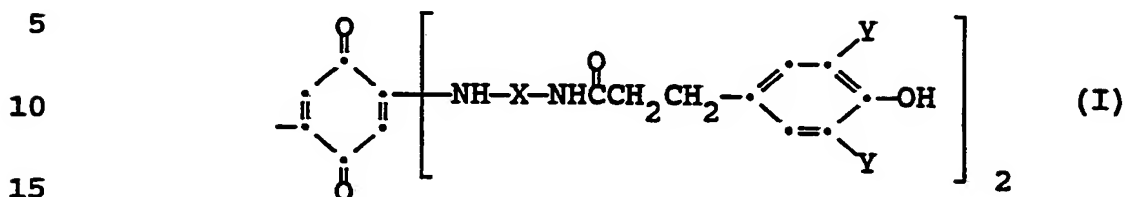
4. A polyolefin composition comprising an intimate mixture of

- 70 (i) a normally-solid polymer of ethylene, propylene, a mixture of ethylene and propylene or polymers of

- 10 -

ethylene and an  $\alpha$ -olefin having 4 to 12 carbon atoms; and

(ii) a compound having the formula:



wherein

X is alkylene or cycloalkylene; and

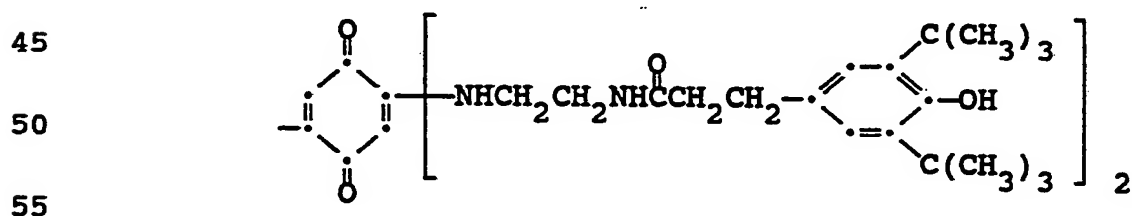
Y is a tertiary hydrocarbyl group having the formula



wherein Z is alkyl or aryl.

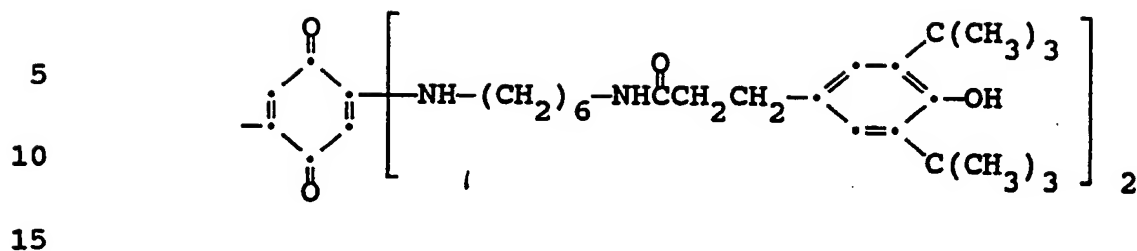
5. A composition according to Claim 4 wherein component (i) is polyethylene and the concentration of component (ii) is 0.1 to 1.0 weight percent based on the total weight of the composition.

6. A composition according to Claim 4 wherein component (ii) is a compound having the formula:

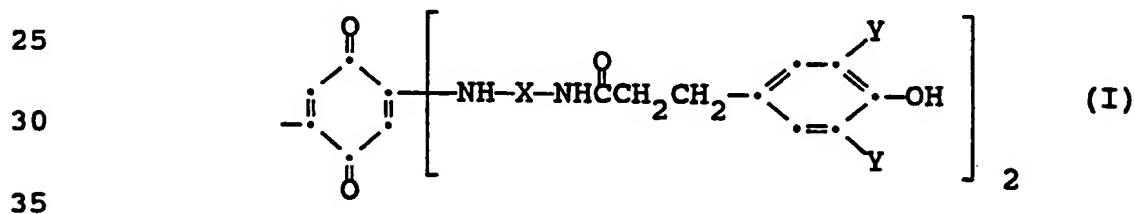


7. A composition according to Claim 4 wherein component (ii) is a compound having the formula:

- 11 -



8. A coated article comprising a copper material bearing a coating of a polyolefin composition comprising
- (i) a normally-solid polymer of ethylene, propylene, a mixture of ethylene and propylene or polymers of ethylene and an  $\alpha$ -olefin having 4 to 12 carbon atoms; and
- (ii) a compound having the formula:



wherein

X is alkylene or cycloalkylene; and

Y is a tertiary hydrocarbyl group having the formula



wherein Z is alkyl or aryl.

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C07C235/34;      C07C235/36;      C08K5/20;      C08L23/02		
<b>II. FIELDS SEARCHED</b> Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C07C ;      C08K ;      C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	FR,A,2 219 182 (BASF AKTIENGESELLSCHAFT) 20 September 1974 see claims	1-8
A	FR,A,2 351 953 (CIBA-GEIGY AG) 16 December 1977 see claims	1-8
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">02 JULY 1993</div>		Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">14. 07. 93</div>
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>		Signature of Authorized Officer <div style="text-align: center; font-weight: bold;">SANCHEZ Y GARCIA J.</div>

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9302722  
SA 72234

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
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02/07/93

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